Oxidation of Zircaloy Fuel Cladding in Water-Cooled Nuclear Reactors

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With the development of higher burn-up fuels for nuclear power reactors, much greater demands are being placed on the performance of the Zircaloy fuel sheaths. The principal threat to the integrity of the sheath is oxidation/corrosion and hydriding, leading to somewhat uniform thinning, and in some instances to localized corrosion in the form of nodular attack and/or hydriding. Failure leads to the release of fission products into the coolant, which in turn contributes to the man-REM costs of operating the system. Extensive fuel failures may require shutdown, which results in the unit being unavailable for normal operation. Thus, strong operational and economic reasons exist for enhancing fuel reliability. The principal goal of the proposed work is to develop sophisticated physico-electrochemical models for the corrosion of Zircaloy fuel sheaths that can be used by reactor operators to *actively manage* the accumulation of damage and thereby minimize the risk of fuel cladding failure in operating reactors.

While the kinetics and mechanisms of the oxidation of zirconium and zirconium alloys have been extensively studied, little effort has been made to develop deterministic (as opposed to empirical and semi-empirical) models that can be used to predict fuel sheath performance and reliability at very high burn-ups in operating reactors. Those attempts at developing algorithms have employed semi-empirical, parabolic, or cubic models (e.g., $L2 = kt + C$, where L is the oxide thickness, t is time, k is the parabolic rate constant, and C is a constant) to extrapolate oxide thickness data to longer times, but the validity of these models is highly uncertain. Furthermore, the models generally ignore the cathodic reaction(s) that occur on the fuel sheath surface and none attempt to model the actual electrochemical conditions that exist within porous deposits at the fuel sheath/coolant (fs/c) interface. Other problems include the simplicity of the diffusion model that predicts parabolic growth, particularly when viewed in light of more modern models

for the growth of anodic oxide films; the inability of the models to predict the transition that occurs in growth kinetics from parabolic (or cubic) to linear at a more-or-less specific oxide film thickness in terms of fundamental, atomic scale processes; the exclusion of effects due to second phase particle (SPPs) on the cathodic processes that occur within the outer layer; the lack of an atomic scale model for the formation of hydrides; and the inability of the present models to describe the influence of solution-phase species, such as $Li+$, on the oxide film growth kinetics. On reflection, it is apparent that the most glaring deficiency in the current theories and models is the lack of a sound electrochemical basis for the corrosion process under free corrosion conditions. By focusing only upon the *oxidation* of zirconium, these models in effect attempt to treat only half of the problem, in that the *cathodic* processes are ignored. Because the cathodic processes must be included in order to satisfy the conservation of charge, the existing models are "non-physical" and hence cannot constitute a deterministic basis for describing the oxidation phenomenon. Furthermore, some evidence exists to suggest that the cathodic reactions, which must occur at the same rate as the zirconium oxidation reaction, may actually control the overall rate, with the apparent dependence of the rate on oxide thickness reflecting the rate of electron transfer across the film.

The issue with respect to the underlying mechanisms of oxidation and hydriding is important and timely, because of the considerable advances that have been made on these subjects over the past several years. For example, work by the authors over the past twenty years, under DOE/BES sponsorship, has developed the Point Defect Model (PDM) for the growth and breakdown of anodic passive films that form on metal surfaces. Recent work has shown that the PDM provides a much better description of oxide film growth than does the classical "high field" model [HFM], and indeed one attempt has

already been made to apply the PDM to the oxidation of Zircalloy-4. Furthermore, the formation of hydride is readily described by the PDM and a strong possibility exists that a unified, predictive model may be developed for oxidation and hydriding.

As noted above, electrochemical effects are almost totally ignored in the current models, but as with all corrosion processes they are actually dominant. Thus, the radiolysis of the coolant produces a number of electroactive species, including H_2, O_2, and H_2O_2, which react at the cladding/environment interface to consume the charge that is produced by the oxidation of the Zircaloy. The conservation of charge requires that the sum of the anodic partial currents due to Zr and H_2 oxidation be equal to that for the reduction of oxygen and hydrogen peroxide and any other reducible species in the system. The potential at which this condition is satisfied defines the corrosion potential (ECP), which is known to have a major impact on the corrosion of materials in reactor coolant circuits. Over the past decade, the author and his colleagues have developed sophisticated models for the radiolysis of water and the electrochemistry of the coolant circuits in boiling water reactors (BWRs) and more recently in pressurized water reactors (PWRs). Similar models will be developed in the proposed work to accurately describe the electrochemical conditions that exist at the cladding/coolant interface. The objectives of this program are to develop fundamentally new mechanisms for Zr oxidation and hydriding in reactor primary coolant environments that address issues arising from the specific chemistry employed (BWR vs. PWR) as well as from reactor-specific issues related to the mode of operation. The mechanisms will include the important phenomenon of boiling within porous CRUD deposits that exist on the fuel surface. This work is expected to yield new technologies for predicting the rate of growth of ZrO_2 on Zircaloy under high burn-up conditions that can be used to the great benefit of the U.S. nuclear power industry. The technologies will be based on recent advances that this team has made in discerning the mechanism(s) of oxidation and hydriding of metals and alloys, as well as on advanced models that will be developed to describe the electrochemistry of reactor coolants at the fuel cladding/coolant interface, in terms of the bulk coolant chemistry, interfacial boiling, and the operating conditions in the reactor. Thus, the goal is to produce a *predictive* model that relates fuel sheath performance to coolant chemistry and reactor operating history, so that an operator can devise the most cost-effective operating strategies that minimize the risk of fuel failure. The technology will be produced in the form of an algorithm that is readily incorporated into power plant computers and hence can be used as both a risk assessment tool and as an operating planning guide.

The proposed research will represent a *major* departure from work being carried out elsewhere, by undertaking the following activities:

- Incorporating the PDM in place of the diffusion models to describe oxide *and hydride* growth

- Incorporating the cathodic reactions that occur at the fuel cladding/coolant interface including the role of intermetallic precipitates in the film as catalytic sites for these reactions

- Incorporating an advanced coolant radiolysis model for estimating the concentrations of electroactive species (O_2, H_2O_2, H_2, etc) at the cladding surface, as a function of the chemistry of the coolant (pH, [Li], [B], [H_2]) and the operating conditions of the reactor

- Including mechanisms (cation vacancy condensation) for passivity breakdown as a means of describing the onset of nodular attack

- Developing a model based upon the generation and annihilation of point defects (oxygen vacancies, cation vacancies, and zirconium interstitials) at the Zircaloy/zirconia and zirconia/solution interfaces to describe the generation of stress in the interphasial region

- Incorporating a model for the concentration of solutes into porous deposits (CRUD) on the fuel under boiling (BWRs) or nucleate boiling (PWRs) conditions, in order to more accurately describe the environment that is in contact with the Zircaloy surface

- Integrating the damage over the operating history of the reactor, including start-ups, shut downs, and variable power operation

- Exploring the electronic structure and measure kinetic parameters for ZrO_2 film growth on Zircaloy under accurately simulated reactor operating conditions; following film growth *in situ* by electrochemical impedance spectroscopy (EIS)/capacitance measurements, while determining the electronic structure by using Mott-Schottky analysis

- Measuring kinetic parameters (exchange current densities and transfer coefficients) for the reduction of oxygen and the oxidation of hydrogen on Zircaloy under prototypical reactor operating conditions to accurately model the cathodic processes that occur on the cladding surface

The output of this project will be a more comprehensive understanding of the oxidation and hydriding of Zircaloy fuel cladding in reactor coolant environments, with particular emphasis on linkage between the plant operating parameters and the damage incurred due to oxidation and hydriding. Additionally, the project will yield a set of models and codes that will be made available to the nuclear power industry for managing the accumulation of corrosion damage to reactor fuel cladding as a function of the coolant chemistry and reactor operating conditions and history.

Finally, the development of the models and codes outlined in this proposal could greatly aid in the development of Generation IV reactors, by exploring water chemistry, materials/environment compatibility, and fuel design options that would minimize corrosion (oxidation and hydriding) damage to fuel cladding under specified operating regimes.